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EVALUATION OF PLASMA CLEANING AND ELECTRON SPECTROSCOPY FOR REDUCTION OF ORGANIC CONTAMINATION

FINAL REPORT

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1.0 SUMMARY

This report summarizes results of work accomplished during JPL Purchase Order No. GU-561461. The overall objectives of this contract were to provide preliminary evaluation of: (1) the feasibility of plasma cleaning Viking Gas-Chromatograph/Mass-Spectrometer (GCMS) surfaces; and (2) the applicability of low-energy electron (Auger) spectroscopy for monitoring organic contamination on GCMS surfaces.

The primary tasks accomplished include: (1) high-temperature/vacuum surface cleaning studies; (2) contamination with a hydrocarbon organic film and microorganisms; (3) plasma cleaning of selected specimens; and (4) Auger analysis of plasma-cleaned specimens. In high-temperature/vacuum surface cleaning studies, various types of metal and metal oxide surfaces were evaluated for cleanliness based on carbon Auger emission. It was found that all surfaces had significant amounts of carbon present, even following chemical cleaning. The carbon could be desorbed by heating to 1000°C in vacuum of 10^{-8} torr; however, carbon was quickly readsorbed upon exposure to air. Plasma cleaning experiments showed that polymerized butadiene and Bacillus subtilis spores, purposely applied to an aluminum surface, could be removed by exposure to an oxygen plasma.

2.0 INTRODUCTION

The Viking spacecraft scheduled to land on Mars in 1976 is programmed to carry a gas chromatograph and mass spectrometer capable of detecting possible organic substances in the Martian environment. To assure that such detection is free of contamination from Earth, a stringent requirement on the cleaning and assembling of parts has been established. Thus, methods of

cleaning as well as determining the degree of cleanliness are of interest.

A reactive gas (plasma) cleaning technique is being developed for NASA by Boeing under contract NAS8-26385[1]. The principle employed in the plasma cleaning process involves oxidation of organic contaminant to volatile products such as CO_2, H_2O, and low molecular-weight organic compounds. Since the oxidation process is accomplished in a vacuum in the order of 10^{-3} to 10^{2} torr, the volatile reaction products produced by the plasma are removed by the vacuum system. Oxygen is normally used as the reactive gas in the plasma cleaning process. An electrodeless, radio-frequency discharge is employed for creating the reactive oxygen species which are required for oxidation of organic contaminants. The inherent ability of the plasma cleaning process to remove all oxidizable organic molecules from a surface, in contrast to solvent cleaning processes which are limited by purity of the solvent itself, prompted the present study.

To properly evaluate the plasma cleaning process, an ultra-sensitive contaminant monitoring technique had to be employed. Based on the initial cleanliness specification for Viking GCMS hardware, it appeared necessary to detect contaminant film thicknesses in the order of a monolayer or less. Low-energy (Auger) spectroscopy was selected for monitoring because of its ability to detect a contaminant equivalent to film thickness as small as 0.1 to 0.01 monolayer. Assuming a thickness per monolayer of 5 Å and a density of 0.7 g/cm^3. these thicknesses are equivalent to a mass of 3.5×10^{-9} to 3.5×10^{-10} g/cm^2, respectively. Since experiments were to be performed with a hydrocarbon contaminant film (polymerized butadiene and bacterial spores), the Auger emission of carbon was selected for monitoring the presence of contaminant.

Auger electron spectroscopy is a powerful technique for the analysis of elemental constituents and contaminants on solid surfaces. Auger spectroscopy works as follows: When a vacancy in the inner shell of an atom is created by electron impact, an outer-shell electron will drop in to fill the vacancy. The deactivation energy may be carried away by another outer-shell electron, called the Auger electron, which has a kinetic energy characteristic of the atomic species involved. The Auger process has a higher probability for lighter elements with smaller deactivation energies. Due to the small mean-free-path of electrons in the solid, only those Auger electrons originating near the surface are detected. Lander[2] was the first to suggest that the Auger electron spectrum could be used to identify the atomic constituents of surfaces. Recently, research work by several authors[3-6] has greatly publicized the application of the technique. A chart of the Auger peak energy versus atomic number can be found in a review paper[7].

3.0 EXPERIMENTAL APPARATUS

A schematic of the test facility used for both deposition of contaminant films and plasma cleaning in the present study is shown in Figure 1. The multipurpose test chamber employs subsystems including the plasma generator, contaminant gas source,ultraviolet light source, proton accelerator, and a residual gas analyzer. Test specimens were mounted on a rotatable water cooled plate at the center of the chamber.

Contaminant films were deposited by irradiating specimens with ultraviolet radiation in a vacuum environment containing butadiene gas. The radiation induced polymerization of a stable organic compound onto surfaces. For this mode of operation, the specimen plate was oriented such that the

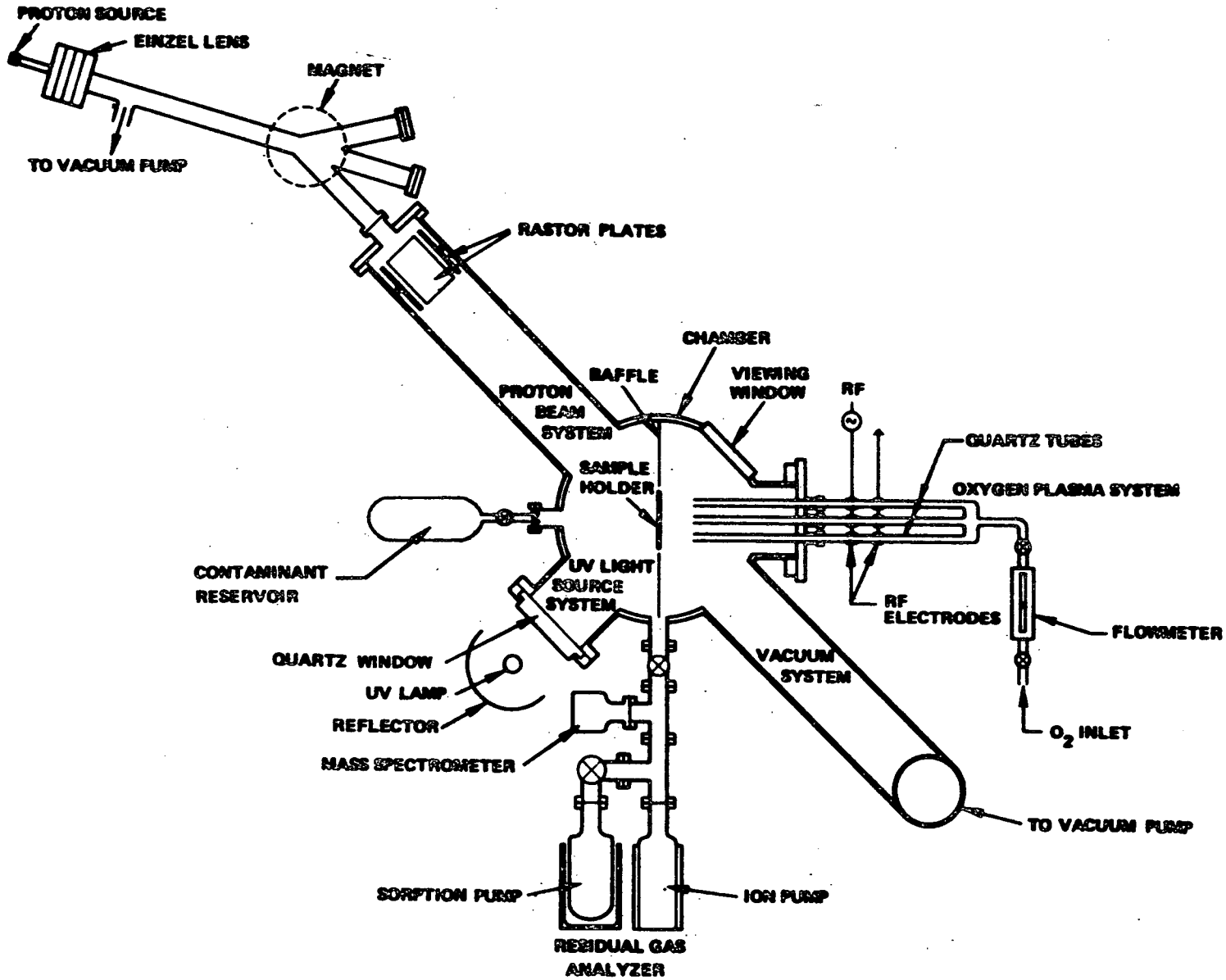

Figure 1: SCHEMATIC OF FACILITY UTILIZED FOR DEPOSITING CONTAMINANT FILMS AND PLASMA CLEANING

specimen was normal to the ultraviolet light source. A General Electric UA-3 mercury-arc lamp provided the ultraviolet radiation for contamination. The ultraviolet intensity at the specimen location was measured to be 7.4 mw/cm^2 (in the wavelength region shorter than about 360 nanometers (nm)). The hydrocarbon monomer used to produce the majority of contaminant films was 1, 3-butadiene, CH_2:CHCH:CH_2. This hydrocarbon gas was chosen because existing literature[8] indicated that it could be uniformly deposited with ultraviolet radiation. The procedure followed to deposit contaminant films involved evacuating the chamber to about 10^{-3} torr, and then backfilling to about 4 torr with the contaminant gas. Contaminant deposition was then initiated by starting the ultraviolet lamp.

Microbial contamination was effected by depositing bacterial spores on the aluminum samples. Approximately 100 spores of Bacillus subtilis, suspended in 0.01 ml ethyl alcohol, were spread onto the surface of the samples and allowed to air dry.

Plasma cleaning was accomplished by exposing specimens to reactive oxygen species, created in an electrodeless rf discharge in a small (4 mm ID) quartz tube. For this operation, the test specimen was oriented normal to the quartz plasma tube, and at a separation of about 10 cm. High purity (99.999 percent) oxygen was introduced into the plasma tube through a suitable flow meter and throttling valve. One tube was used in the present experiments, although three are available on the facility as shown in Figure 1. Pressures at the inlet to the quartz tube and in the chamber were about 1 torr and 5×10^{-4} torr, respectively. An oxygen flow of about 35 STP cm^3/min was used. An rf electrode arrangement and a suitable gas flow which

would allow the electrical discharge to occur at the end of the plasma tubes were established by experimentation. This mode of operation minimized recombination of atomic oxygen on tube walls. The rf power input used was 20 watts/tube at a frequency of 13.56 mHz.

The electron spectrometer[9] used for contaminant detection is a display-type 3-grid LEED optics housed in an ion-pumped ultrahigh vacuum system with an ultimate vacuum of ~1 x 10^{-10} torr. The circuitry and operational procedures for Auger analyses were similar to those described in the literature[4,5]. For the present work, the Auger spectrum was taken with a 2KeV primary beam of 1.5 μ A current delivered by the LEED gun at normal incidence to the surface. The retarding grid was modulated by an a.c. voltage of 6.5 V peak-to-peak amplitude at 400 Hz. Scattered electrons were detected with a phase-sensitive detector operated at 800 Hz. The output of this detector is proportional to the second derivative of the retarding-field I-V curve, customarily referred to as dN(E)/dE. The spectra presented in this work for kinetic energy above about 100 eV were all taken with the same sensitivity. Below that energy, spectra were taken under reduced sensitivities as indicated.

It was noted that the resolution of the retarding-field method is about 2% of the kinetic energy of the electrons. Therefore, an Auger peak at 100 eV may be well defined whereas another one at 500 eV may be smeared. (The instrumentation can definitely be improved. For example, a much superior version of the Auger analyzer based on the design of Palmberg, Bohn and Tracy[6] is commercially available.) Furthermore, an Auger signal depends on factors such as cross section for inner-shell ionization, Auger yield efficiency, escape probability, substrate reflectivity, surface topograph, surface condition, etc. Thus, the magnitude of the Auger signal in the absence of a rigorous calibration can only be interpreted qualitatively.

4.0 RESULTS AND DISCUSSION

The overall experimental plan to evaluate the plasma cleaning process involved: (1) preparing specimens which were contamination-free; (2) determining whether specimens would be re-contaminated upon exposure to air; (3) purposely depositing hydrocarbon and microorganism contaminants, plasma cleaning, and determining whether the contaminants were removed.

In general, considerable difficulty was encountered in preparing contamination (carbon)-free specimens for subsequent plasma cleaning experiments. Mechanical problems with the ion gun prevented sputter-cleaning from being performed. An alternative technique (heating in high vacuum) was not effective for removing carbon on aluminum specimens. Furthermore, it was found that exposure to air for a brief period following cleaning, induced re-contamination (with carbon). In subsequent plasma cleaning experiments, it was shown that the Auger spectrometer could detect the additional carbon applied during contaminant application, and that the plasma cleaning process could remove the contaminant (to the limit of resolution imposed by the background carbon signal). Detailed results of numerous experiments aimed at preparing carbon-free surfaces for cleaning experiments follow.

Figures 2 and 3 show the Auger spectra from a steel plate and a molybdenum plate, respectively, at several stages of heat treatment. The temperature was calibrated separately with an optical pyrometer and a thermocouple with an accuracy of about $\pm$ 5%. These surfaces (parts of an indirect heater assembly for the LEED experiment)[9] had previously undergone several cycles of heating to 1000°C in vacuum of 10^{-8} torr, and then exposure to air. The Auger results are reproducible. In Figure 2 it can be seen that the as-inserted steel plate yields signals of carbon (270 eV) and oxygen (515 eV) as major

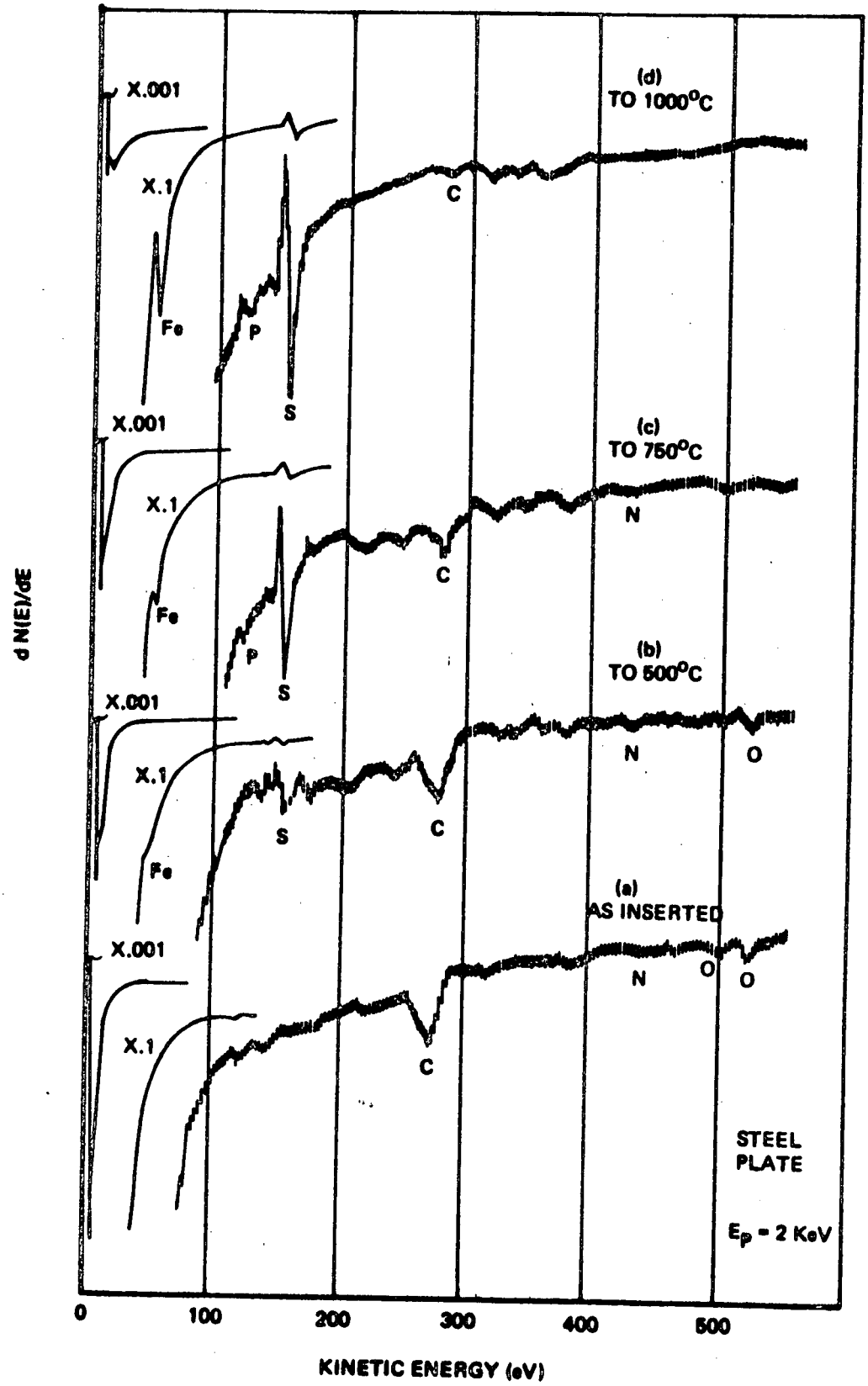

Figure 2: AUGER SPECTRA OF A STEEL PLATE AT SEVERAL STAGES OF HEAT TREATMENT

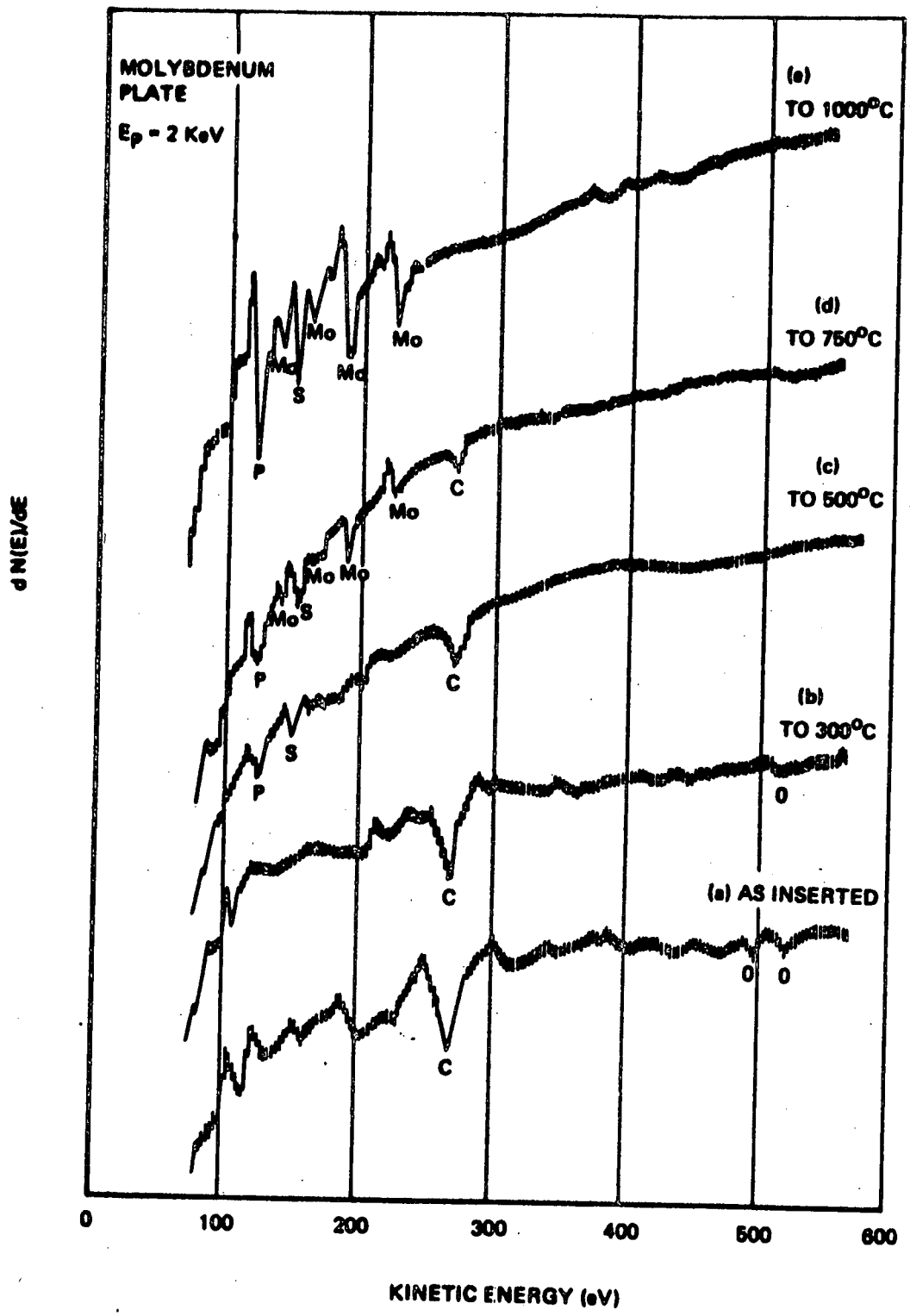

Figure 3: AUGER SPECTRA OF A MOLYBDENUM PLATE AT SEVERAL STAGES OF HEAT TREATMENT

components in the spectrum. The surface contamination is reduced by heating to higher and higher temperatures while signals of iron (48 eV), sulphur (150 eV) and phosphorus (120 eV) gradually become prominent. The chemical state of carbon on the as-inserted surface is undetermined. Most likely it may be from adsorbed CO, CO_2 and organic compounds. Sulphur and phosphorus are probably bulk impurities which segregate to the surface upon heating.

It is of interest to estimate the amount of carbon present on the surface of the as-inserted steel plate. The fact that the iron signal at 48 eV was not detected in Figure 2a, suggests that the adsorbed surface contamination is at least 2 to 3 monolayers thick (judging from the escape depth of the Auger electrons)[5]. Moreover, the carbon Auger signal in Figure 2a is very comparable with that obtained from a graphite sample. In the latter case, if it is assumed that the carbon Auger signal at 270 eV represents 3 monolayers, then the magnitude of the signal would correspond to ~0.2 $\mu g/cm^2$ of carbon. After heating the steel plate to 1000°C, the residual carbon is probably less than ~0.02 $\mu g/cm^2$ (Figure 2d).

Half of the secondary electron peak from the steel plate is plotted at a sensitivity of 0.001 in Figure 2. With the reduction of surface contamination by heating, the secondary yield decreases. This is consistent with earlier work in the field of secondary emission.[10]

Auger spectra of a molybdenum plate at several stages of heat treatment are shown in Figure 3. Similar to the results from the steel plate, the as-inserted sample was contaminated mainly by carbon-containing materials. Heating the sample to approximately 1000°C in vacuum eliminated the carbon signal. Meanwhile, signals from Mo, S and P become prominent. Sulphur and phosphorus are probably bulk impurities.

The observation that heat treated surfaces of steel and molybdenum become recontaminated with carbon upon exposure to ambient atmosphere is reasonable to expect. Each atom on a solid surface would suffer approximately 10^9 collisions per second from molecules in air at standard conditions. If a certain carbon-containing gas has a unity sticking coefficient and a pressure of 10^{-6} torr, it would cover the surface to one monolayer in one second.

Auger spectra from an as-inserted gold film and its ceramic substrate are shown in Figure 4. (The gold film was deposited in a vacuum system equipped with an oil diffusion pump.) In addition to the gold signals, the Auger peak of carbon is the main feature of the spectrum. In fact, similar experiments on etched silicon wafers, evaporated germanium films and several other surfaces have all yielded evidence that carbon is the major contaminant on the surface.

Because of a special interest in aluminum surfaces in the present contract, 16 sets of Auger spectra were collected from eight samples by examining two different locations on each sample (purity 99.99%, dimensions 6 x 12 x 1 mm). Four samples were subjected to different surface preparation procedures and then examined by the Auger technique. The four different preparation procedures are described as follows:

1. Electro-polished in a solution containing 70% H_3PO_4, 12% acetic acid, 3% HNO_3 and 15% water at 65°C, using another piece of aluminum as the cathode. Electro-polished at 7V and 1.5 A for 5 minutes, and then rinsed with distilled water.
2. Etched in a solution containing 30% H_2SO_4, 3% $Na_2Cr_2O_7$ and 67% water at 60°C for 20 minutes, and then rinsed with distilled water.

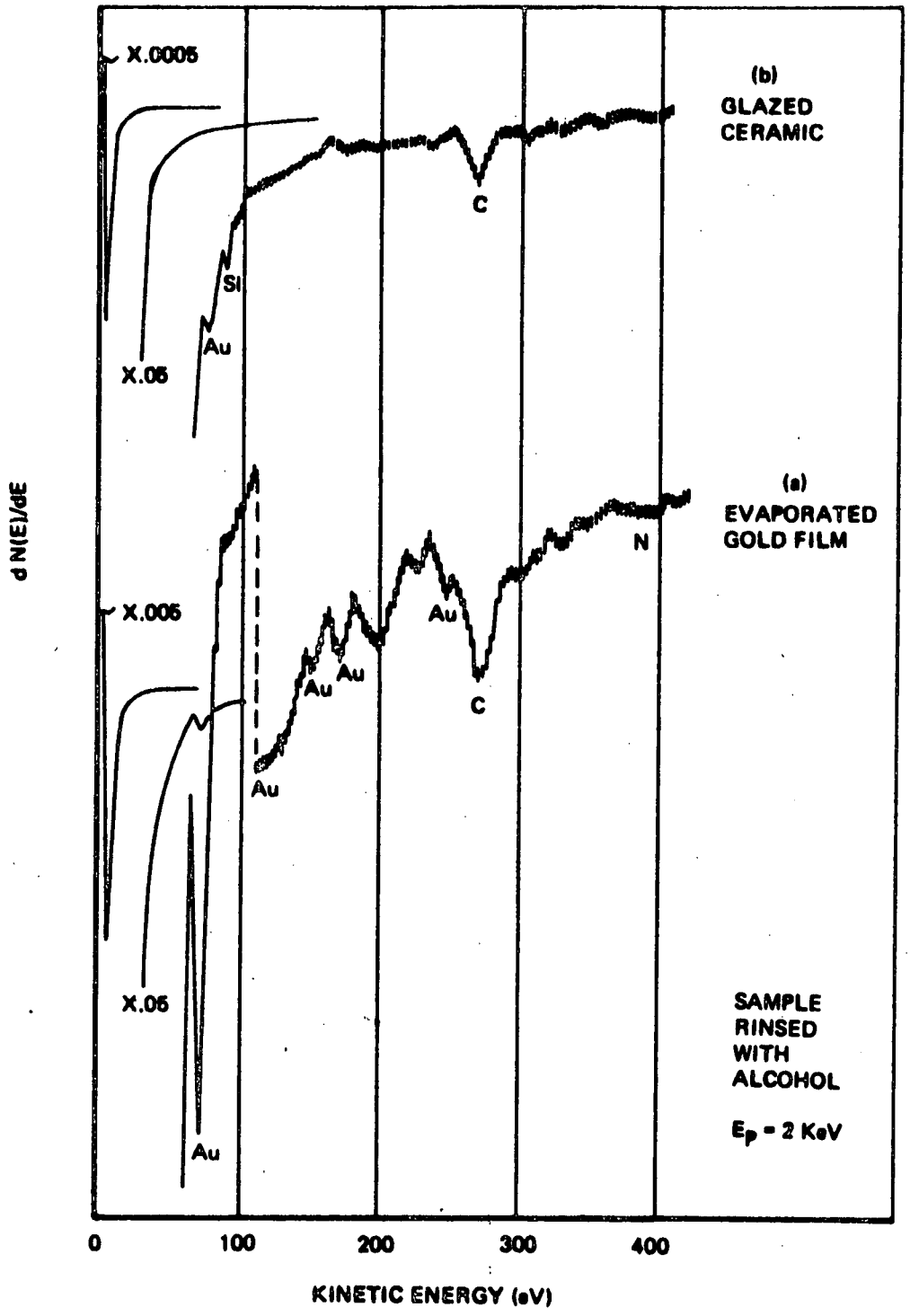

Figure 4: AUGER SPECTRA OF AN EVAPORATED GOLD FILM AND A GLAZED CERAMIC SURFACE

3. Etched in 1M solution of NaOH for 1 minute, washed with 50% HNO_3, and then rinsed with distilled water.

4. Electro-polished and then etched as described in 1 and 3 above.

Invariably, Auger signals of aluminum (52 eV), oxygen (515 eV) and carbon were detected. In addition, a charging phenomenon was observed in the spectra of the as-inserted aluminum sample. Figure 5 shows the Auger spectra from an electro-polished surface (preparation procedure No. 1). Note that a feature (denoted by a question mark) actually migrated to higher energies as the surface was being bombarded by the primary electron beam. This feature is attributed to a loosely adsorbed layer containg carbon because: (a) it resembles the line shape of the carbon signal, and (b) a carbon peak eventually appeared at 270 eV (probably due to polymerization of the carbon containing materials). In general, it was found that aluminum specimens from an ordinary environment were always covered by a layer of oxide[11]. The bulk Al_2O_3 is an insulator[12]. It was also found that a NaOH etch (preparation procedure No. 3) yields surfaces with the strongest Al and O signals.

Four additional aluminum samples were etched with NaOH and purposely contaminated with butadiene polymer by irradiating with ultraviolet radiation for 5 minutes. Two of these specimens were additionally contaminated with deposits of Bacillus subtilis spores. After Auger analyses, the contaminated samples were cleaned in an oxygen plasma for 60 minutes at an approximate pressure of 5×10^{-4} torr. The surfaces were then examined with Auger spectroscopy again. Typical results from these analyses are shown in Figure 6. It was noted that the butadiene contamination was sufficiently

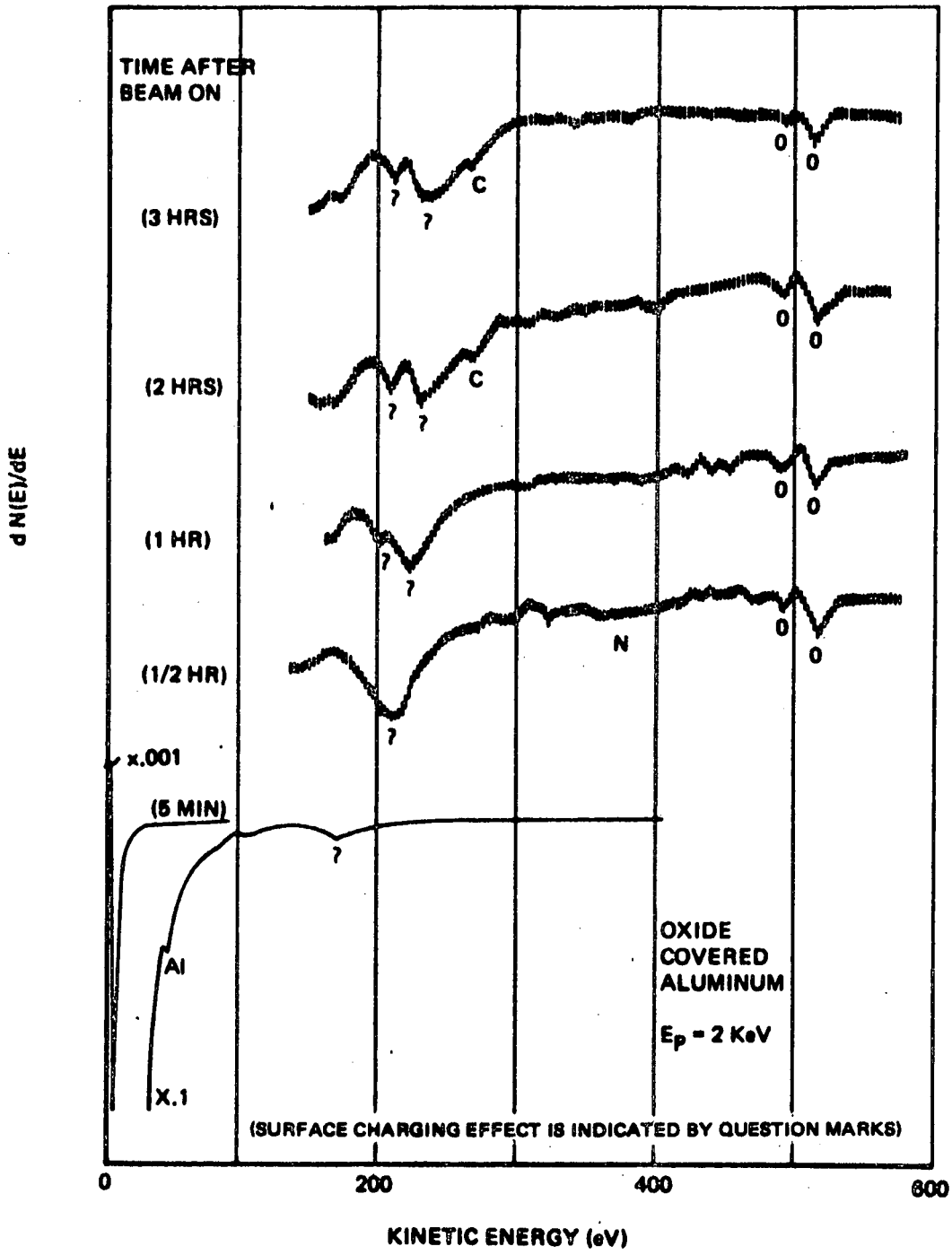

Figure 5: AUGER SPECTRA FROM AN ELECTRO-POLISHED ALUMINUM SURFACE

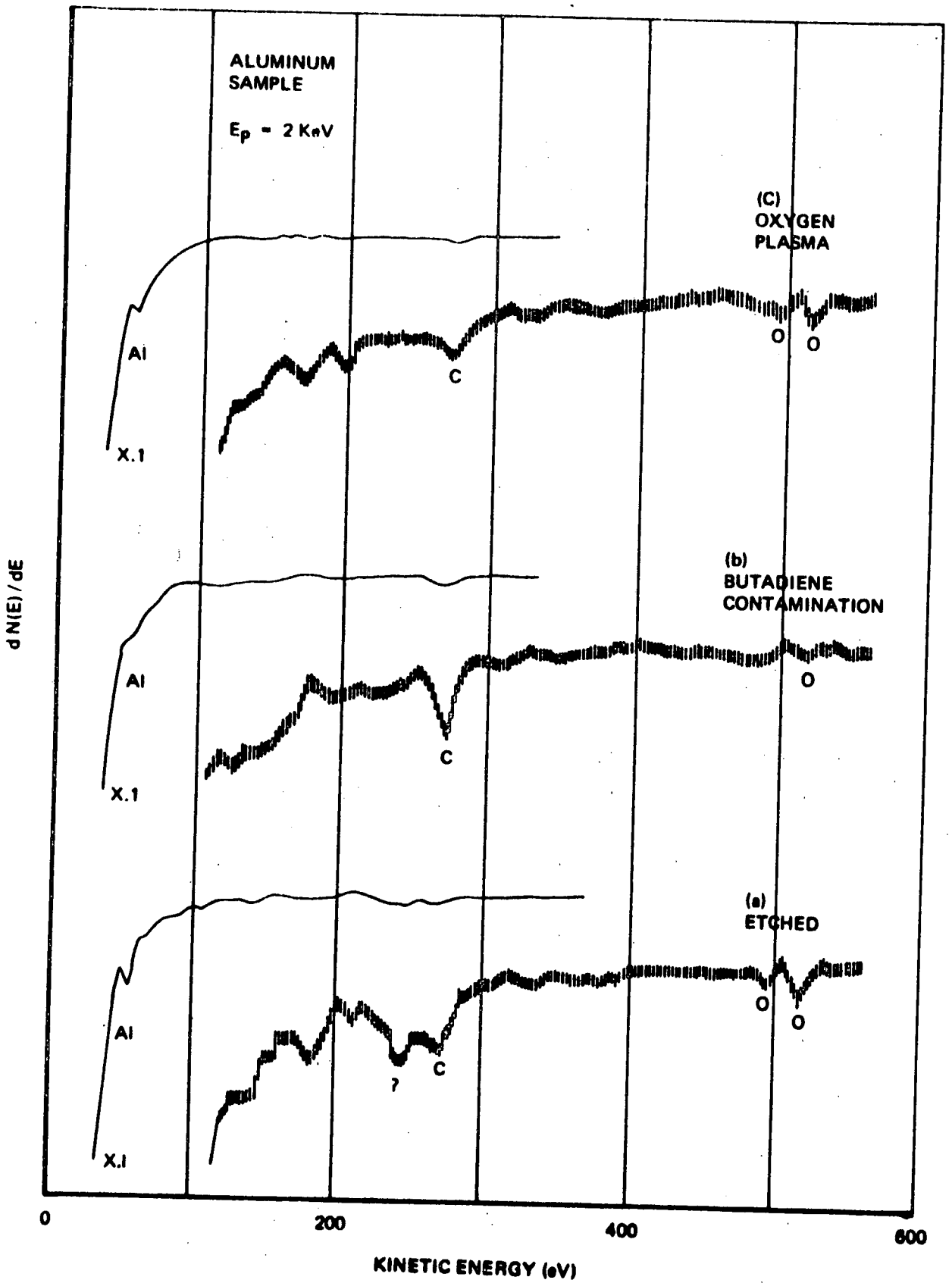

Figure 6: TYPICAL AUGER SPECTRA FROM ALUMINUM SURFACES AFTER CHEMICAL ETCHING, BUTADIENE CONTAMINATION, AND OXYGEN PLASMA CLEANING

thick to suppress both Al and O signals (implying a thickness in excess of several monolayers). Also, the carbon signal became more prominent and the charging phenomenon disappeared. After plasma cleaning, the carbon signal decreased and both Al and O signals were somewhat restored, implying removal of contaminant. The residual carbon signal in the spectrum of Figure 6c may be due to either residual carbon from the plasma cleaning process or re-contamination during transit through air. Similar results were obtained on all four contaminated specimens.

5.0 CONCLUSIONS

The following conclusions can be made as a result of research performed in this contract.

1. Auger spectroscopy can be used for monitoring organic contamination on surfaces where sensitivity for monolayer-magnitude coverage is required.

2. Analysis for carbon Auger-electron-emission from a contaminant film is complicated by the presence of adsorbed carbon from atmospheric gases.

3. Exposure of contaminated surfaces to an oxygen plasma can reduce the carbon Auger emission to the background level expected from adsorbed atmospheric gases. This shows that the plasma cleaning technique is an effective method for removing both organic films and microbial contamination.

6.0 RECOMMENDED FOLLOW-ON WORK

The data presented in this report demonstrate the plasma cleaning technique to be highly effective for removing organic films and microbial removal. Previous Boeing data show the plasma process to be equally effective for sterilizing. These latter data have shown "D-values" to range from 1.7 to 5.0 minutes for Bacillus subtilis spores under plasma operating conditions. Because of these results, it appears likely that plasma sterilization would be desirable for various planetary quarantine applications including prelaunch decontamination of instruments, inflight sterilization and back contamination consideration. The process desirability is enhanced by the fact that sterilization can be accomplished at relatively low temperatures (approximately 50°C) and can utilize inert gases.

The plasma sterilization data obtained to date by Boeing have demonstrated the feasibility of the technique. However, a number of investigations remain to be accomplished if the process is to be applied to spacecraft systems. It is recommended that these investigations be implemented as a follow-on to this contract. A list of recommended research task follows.

Task I - Range of Plasma Biological Effects

Objective: To determine the lethal effect of plasma on diverse types of organisms including various bacterial species, viruses and fungi.

Task II - Plasma Lethality Mechanism

Objective: To determine the elements of the plasma that are responsible for microbial death by electron microscopic scanning, plasma spectral photometric studies,

plasma density studies, temperature variations, etc.

Task III - Plasma Penetration

Objective: To determine the effectiveness of plasma gas penetration into surfaces, including mated surfaces; examples being stacked layers, cylinders (tubing) of various diameters and lengths, packaged materials, fiber or wire bundles, etc.

Task IV - Plasma Gas Effects

Objective: To determine the relative lethal effects of various gases and combination of gases including nitrogen, helium, air, argon + carbon dioxide, argon + nitrogen, etc.

Task V - Material Compatibility

Objective: To determine plasma compatibility with spacecraft materials, including epoxies, plastics, thermal coatings, etc.

Task VI - Sterilization Chamber Design

Objective: To determine the sterilization chamber configuration, size, and internal surface characteristics necessary for optimum plasma effects.

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